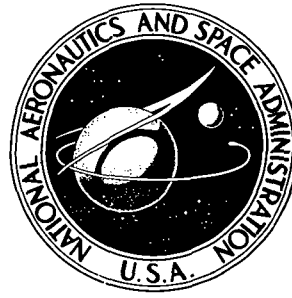


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EFFECT OF NATURE
OF OXYGEN INTERACTIONS
ON FRICTION OF TITANIUM,
ALUMINUM, AND MOLYBDENUM

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16. Abstract <p>Friction studies were conducted with a gold pin contacting titanium, aluminum, and molybdenum surfaces after exposure to oxygen with various methods. Oxygen was adsorbed on the surface, it reacted with the surface, and the surface was ion bombarded with oxygen. The presence of oxygen was monitored with Auger spectroscopy. Titanium friction varied with the mode of the metal-oxygen interaction. It was highest with the adsorbed oxygen and least with ion bombardment using oxygen. Aluminum exhibited lower friction values for the reacted and the ion bombarded surfaces than for the surface having the adsorbed layer. With molybdenum the friction coefficients were generally the same despite the nature of the surface treatment with oxygen.</p>					
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EFFECT OF NATURE OF OXYGEN INTERACTIONS ON FRICTION

OF TITANIUM, ALUMINUM, AND MOLYBDENUM

by Donald H. Buckley

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SUMMARY

Sliding friction experiments were conducted with a gold pin contacting titanium, aluminum, and molybdenum after their exposure to and interaction with oxygen. The surface treatments examined included oxygen adsorption, chemical reaction with oxygen, and bombardment with oxygen ions. Friction experiments were conducted in vacuum to eliminate the effects of environmental adsorbates, and Auger emission spectroscopy was used to monitor the presence of oxygen.

The results of the investigation indicate that with titanium the mode of oxygen interaction with the surface affects friction. The friction coefficient for titanium was highest with the adsorbed film, intermediate with the reacted film, and lowest on the surface ion bombarded with oxygen ions. With aluminum, friction results were essentially the same for the reacted and ion bombarded surfaces, but the surface with the adsorbed film exhibited higher friction coefficients. For molybdenum, the friction coefficient was essentially the same for all three surface oxygen treatments.

INTRODUCTION

Titanium has notoriously poor friction and wear behavior. It exhibits a strong tendency to gall and seize when in sliding or rubbing contact (ref. 1). Furthermore, wear particles from rubs, for example, with titanium, can react violently with oxygen resulting in ignition sources for combustible gas mixtures.

The desirable mechanical properties and the weight considerations of titanium and titanium alloys make these materials strong candidates for mechanical components in advanced aircraft design. Some effort directed toward reducing the adhesion, friction, and wear of titanium and titanium alloys therefore is warranted.

The objective of the present investigation was to examine surface treatments of ele-

mental titanium which will result in reduced adhesion and friction. A companion report (ref. 2) deals with lubricants for titanium surfaces. The surface treatments examined included oxygen adsorption, chemical reaction with oxygen, and ion bombardment of titanium with oxygen ions. Data were also obtained with aluminum and molybdenum. Clean titanium, aluminum, and molybdenum surfaces were generated in a vacuum system by argon ion bombardment; the surfaces served as the initial surface condition for treatment. LEED (low energy electron diffraction) and Auger emission spectroscopy analyses were used to monitor surface structure and chemistry. Adhesion and friction experiments were conducted with a pin on a disk specimen configuration.

MATERIALS

The purity of the titanium used in this investigation was 99.97 percent with the principal impurity being oxygen. The purity of the molybdenum was 99.99 and that of the aluminum was 99.999 percent. The oxygen was reagent grade.

The titanium, aluminum, and molybdenum were all single crystals. The titanium flat disk surface was the (0001) orientation $\pm 2^\circ$. The molybdenum was of the (110) orientation and the aluminum the (100) orientation $\pm 2^\circ$. The gold pin had a radius with a (111) orientation $\pm 2^\circ$.

APPARATUS

The apparatus used in this investigation was a vacuum system having built into it the capabilities for measuring adhesion, load, and friction. The apparatus also contained the surface analytical tools, Auger and LEED analyses. The mechanism for measuring adhesion, loading, and friction is shown schematically in figure 1.

The titanium, aluminum, and molybdenum flats were 12 millimeters in diameter. The gold pin had a 3-millimeter diameter with a 2-millimeter radius on one end.

A gimbal mounted beam projected into the vacuum system. The beam contains two flats machined normal to each other with strain gages mounted thereon. The end of the rod contains the gold single crystal pin specimen. As the beam is moved inward toward the disk a load is applied which is measured by the strain gage. If adhesion occurs when the load is removed, the adhesion forces are measured by the deflection of the beam in the direction opposite to which the load was applied (see fig. 1).

The vertical sliding motion of the pin along the disk surface is accomplished through a motorized gimbal assembly. Under an applied load, the friction force is sensed by the strain gage normal to that used to measure load.

Almost any sensitivity desired can be achieved by properly thinning the flats in the beam containing the strain gages. In the present study, a 0.1-newton force resulted in full-scale deflection on a conventional strip chart recorded with load, adhesion, or friction force.

Multiple wear tracks could be generated on the disk specimen surface by translational motion of the beam containing the pin. This feature was used to examine the friction coefficient at various loads. Pin sliding was in the vertical direction as shown in figure 1.

The vacuum apparatus in which the components of figure 1 were contained also had a LEED system and an Auger spectrometer. The electron beam from both LEED and Auger spectroscopy could be focused on any disk site desired.

The disk specimens were titanium, aluminum, and molybdenum. In this investigation the pin was always gold.

EXPERIMENTAL PROCEDURE

The disk specimens were polished down on metallurgical papers to 600 grit and were then electropolished. The specimens were placed in the vacuum friction and wear apparatus and the system evacuated and subsequently baked-out to achieve a pressure of 1.33×10^{-8} newton per square meter (10^{-10} torr). When this pressure was achieved, argon gas was bled back into the vacuum chamber to a pressure of 10 micrometers. A 1000-volt potential was applied and the specimen argon sputter bombarded for a period of 30 minutes.

After 30 minutes the vacuum chamber was reevacuated and Auger spectra were obtained of the surface to determine the degree of surface cleanliness. When clean, as determined by LEED and Auger spectroscopy, adhesion and friction experiments were conducted.

Loads of from 1 to 30 grams were applied to the pin-disk contact by deflection of the beam of figure 1. Both load and friction force were continuously monitored during a friction experiment. Sliding velocity was 0.7 millimeter per minute with a total sliding distance of 0.7 millimeter.

RESULTS AND DISCUSSION

Titanium

An Auger spectrum of the single crystal titanium surface was obtained prior to sputter cleaning. The crystal was as received after electropolishing and after bake-out

of the vacuum system. In figure 2(a), in addition to the titanium Auger peaks indicated, both carbon and oxygen are seen on the surface.

Figure 2(b) is the Auger spectrum for the titanium surface after sputter cleaning. The carbon peak has completely disappeared from the spectrum leaving only titanium and a small oxygen peak. The residual oxygen may arise from the bulk contamination of titanium.

In figure 2(c) the titanium surface of figure 2(b) was exposed to oxygen at 10 micrometers of pressure and 23° C for a period of 1 hour to ensure surface saturation. Note the oxygen peak height as compared to those for the titanium.

Figure 2(d) is an Auger spectrum for titanium which had been exposed to oxygen at 10 micrometers for 1 hour and 500° C. The titanium surface was blue in color indicating the rutile oxide structure TiO_2 on the surface (refs. 3 and 4). If the oxygen peak height is compared to those of the titanium peaks and the corresponding peaks in figure 2(c), it can be seen that more oxygen is present on the surface with the oxide than with the simple adsorbed film of figure 2(c).

An argon sputter cleaned titanium surface was next bombarded with oxygen ions (ref. 5) at a 1000-volt potential for 1 hour. The relative titanium and oxygen peak heights obtained in the Auger spectrum are presented in figure 2(e). The oxygen to titanium peak height ratios in figure 2(e) indicate that the surface accommodated as much or slightly more oxygen with oxygen ion bombardment than with either adsorption or chemical reaction to form an oxide.

Friction data were obtained for the titanium surfaces as a function of load for the surfaces with adsorbed, reacted, and ion bombarded oxygen ions. The results obtained are presented in figure 3.

In figure 3 at loads of 1 and 3 grams, the adsorbed film gave the highest friction coefficients, the reacted oxide film of TiO_2 intermediate values at light loads, and the ion bombarded surfaces the lowest friction coefficients. Minimum friction over the entire load range was obtained with the oxygen ion bombarded surface.

Titanium under certain conditions oxidizes with a TiO layer between the metallic surface and the TiO_2 layer where oxidation times and temperatures are such as to impart the blue color to the rutile surface (ref. 4). Thus, for the reacted surface film there is the metallic surface which is covered by a TiO layer. Because of the solubility of oxygen in titanium metal the TiO layer adheres poorly to the titanium. Above the TiO layer is the TiO_2 outer or surface layer.

ESCA (electron spectroscopy for chemical analysis) experiments with molybdenum indicate that with normal oxidation there is a layer of MoO_2 on the metallic molybdenum surface between the metal and the outer MoO_3 layer. Bombardment of that surface results in conversion to almost pure MoO_3 (ref. 6). Titanium may behave in an analogous manner. This would account for the increased oxygen to titanium ratio of figure 2(e)

when compared with figures 2(c) and (d).

The oxidation of titanium results in the diffusion of oxygen into titanium producing a hardening effect in the surficial region of the metal below the oxide layer. The depth to which hardening will occur depends strongly on oxidation conditions including temperature, pressure, and time. Figure 4 presents a family of curves for the subsurface microhardness of titanium after oxidation at 1×10^5 newtons per square meter of oxygen and 900°C for various periods of time. These data were obtained from reference 3.

A series of titanium specimens was oxidized at 1×10^5 newtons per square meter of oxygen and 900°C for the time periods indicated in figure 4 (see ref. 3 for mechanisms of titanium oxidation at 900°C). The oxide scales were removed. Microhardness measurements were then made and differences in hardness were found to exist. The longer the oxidation time the higher the hardness.

Eberhard microhardness indentations were made on annealed unoxidized specimens, oxygen ion implanted specimens, and those oxidized for various time periods (see fig. 4). The results of these measurements are presented in figure 5. In figure 5 hardness differences are plotted as functions of time for the oxidized samples. The oxygen ion bombarded specimens did not harden as did the oxidized specimens (see ordinate of fig. 5).

The fact that ion bombardment of titanium with oxygen did not produce the embrittling effects observed with oxidation is significant. From the view of mechanical property considerations the hardening of titanium by oxygen may result in considerable embrittlement of the surface layer. Furthermore, ion bombardment affords the surface reduced friction (fig. 3).

Under certain conditions the oxidized titanium shows marked changes in friction behavior with oxygen exposure. In table I, friction coefficients for titanium as functions of oxygen exposure at 200°C are presented for 1 and 10 gram loads after the removal of the oxide scale. The data indicate that with increasing oxygen exposure time (at both loads) the friction coefficient decreases; this indicates that increasing oxygen diffusion time is beneficial. The increased exposure has two effects: (1) it increases the oxygen concentration in the surficial layers, and (2) it increases surficial hardness. It is of interest to note, however, that hardness per se does not appear to be too significant since the ion implanted specimen gave lower friction than the oxidized specimens even though it did not display the same increase in hardness.

In figure 6 the coefficient of friction is plotted as a function of load for two oxidation times of the titanium. As the load is increased, the friction coefficient for the 10-minute exposure approaches that of the longer 400-minute exposure for those specimens which were treated by oxidation at 900°C followed by removal of the oxide scale.

Aluminum

Aluminum forms a thin, dense, tenacious surface oxide. Anodizing an aluminum surface reduces considerably the tendency for aluminum to seize or gall. In order to gain some insight into the effect of various methods of oxygen exposure on friction an aluminum surface was sputter cleaned. An Auger spectrum of this clean reference surface is shown in figure 7.

The aluminum surface was treated for 30 minutes at 23⁰ C and 10 micrometers to assure oxygen adsorption to saturation, heated in oxygen at 500⁰ C (fig. 8(a)), and ion bombarded with oxygen (fig. 8(b)). In figure 8(a) the Auger spectrum is presented for the oxidized aluminum, and in figure 8(b) the Auger spectrum is for the aluminum ion bombarded with oxygen ion. Note the oxygen peak not present in figure 7 appears in figures 8(a) and (b).

Friction experiments were conducted on the aluminum specimens with adsorbed oxygen, reacted oxygen, and oxygen implanted by ion bombardment. The friction coefficients obtained for these specimens at various loads are presented in figure 9. The data of figure 9 indicate that the friction coefficients for the surface with an adsorbed film are considerably higher than for the reacted and ion bombarded surfaces. The friction coefficients, at various loads, for both the reacted and ion bombarded surfaces are represented by a single curve indicating a decrease in friction coefficient with an increase in load.

The data of figure 9, unlike those of figure 3 obtained with titanium, show no difference in friction behavior between the reacted and ion bombarded surfaces with the exception of the data points at the 1-gram load. In figure 3 friction coefficients were lower for the bombarded surface.

Molybdenum

Molybdenum oxidizes readily and does not form a protective surface oxide layer as is seen with aluminum (ref. 7). Molybdenum trioxide is volatile at moderate temperatures while aluminum and titanium oxides are not. It may be possible to obtain a stable oxide through implantation. Thus, the effectiveness of ion bombardment with oxygen is of interest with a metal like molybdenum.

The same basic oxygen exposures given to titanium and aluminum were given to molybdenum. These consisted of adsorption of oxygen, reaction with oxygen, and ion bombardment with oxygen. The parameters employed were the same as those used with titanium and aluminum.

In figure 10 an Auger spectrum is presented for molybdenum bombarded with oxy-

gen. The oxygen to molybdenum ratio is higher than was observed for adsorbed oxygen, yet the friction results were essentially the same with all three treatments as indicated in figure 11.

An examination of figure 11 indicates no essential difference in friction coefficients with the three different types of exposure to oxygen. A marked increase in friction occurs when the load is increased from 3 to 5 grams. Beyond 5 grams very little change in friction occurs.

Marked differences in friction behavior occur for the three metals titanium, aluminum, and molybdenum. With titanium, the friction coefficient was lowest with oxygen ion bombardment, intermediate with a reaction film, and greatest with the adsorbed film. With aluminum above a 1-gram load, the reacted and ion bombarded films gave comparable friction results while that for the adsorbed film was higher at all loads. The friction coefficients obtained with a molybdenum surface were essentially the same with all three surface treatments.

SUMMARY OF RESULTS

Based on the sliding friction experiments conducted in this investigation with titanium, aluminum, and molybdenum exposed to oxygen in various forms, the following summary remarks are made:

1. The effect of oxygen in reducing the friction of metals such as titanium is a function of the manner in which the oxygen interacts with the surface. Friction was highest with an adsorbed film, intermediate with a reacted film, and least with an ion bombarded surface.
2. With aluminum, above a 1-gram load the friction coefficients for both reacted and oxygen ion bombarded surfaces were comparable, both values were lower than those obtained with adsorbed films at all loads.
3. Molybdenum metal was insensitive to the mode of oxygen interaction with the surface. Adsorbed, reacted, and oxygen ion bombarded surfaces all gave comparable friction coefficients at any one load.
4. Oxygen ion bombardment of titanium with oxygen did not harden the titanium to the extent observed with oxidation.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, September 26, 1975,
506-16.

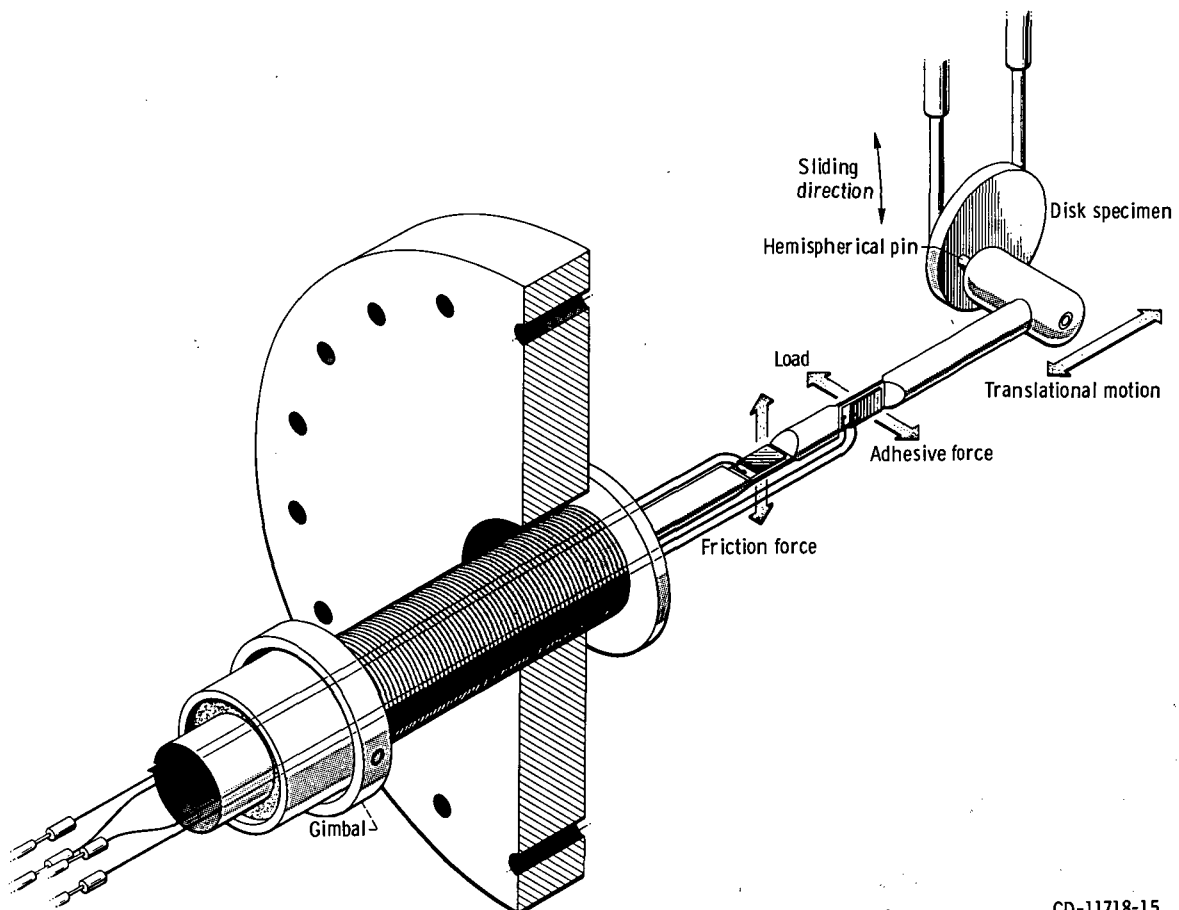
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TABLE I. - FRICTION COEFFICIENT
FOR TITANIUM AT TWO DIFFERENT
LOADS AFTER OXYGEN EXPOSURE

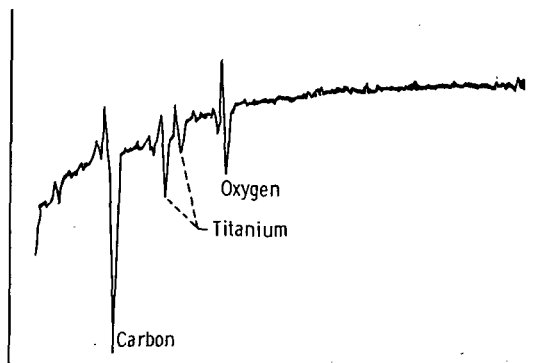
[Exposure - 900°C ; $1 \times 10^5 \text{ N/m}^2$
oxygen; oxide scale removed.].

Oxygen exposure, min	Load, g	
	1	10
	Friction coefficient	
10	5.0	2.0
30	1.0	1.5
90	1.0	1.5
240	1.0	1.0
400	.5	1.0

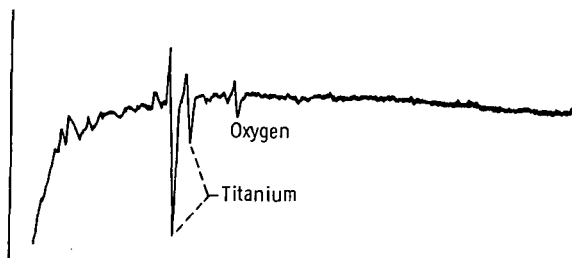


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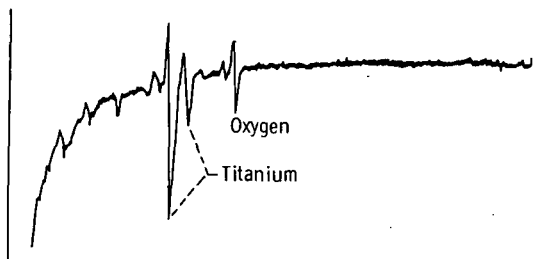
Figure 1. - High-vacuum friction and wear apparatus.



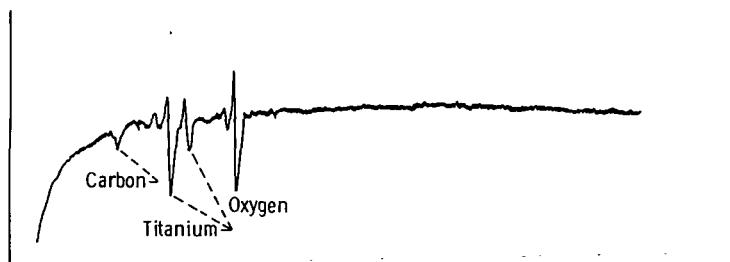
(a) Before sputter cleaning.



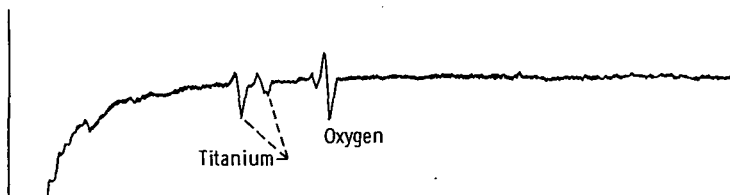
(b) Sputter cleaned.



(c) Adsorbed oxygen.



(d) Oxide film.



(e) Oxygen ion bombarded.

Figure 2. - Auger spectrum for titanium (0001) single crystal surface.

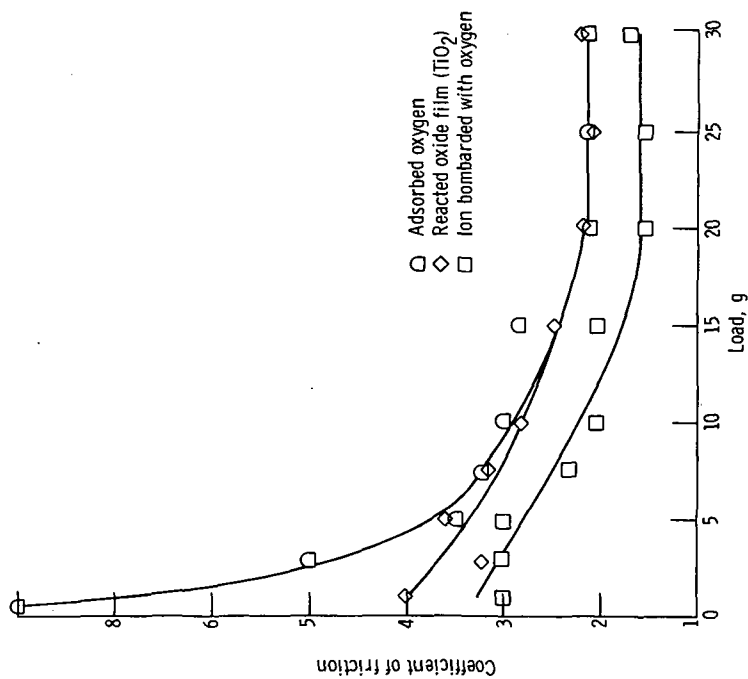


Figure 3. - Coefficient of friction at various loads for titanium (0001) single crystal surface given three different exposures to oxygen. Sliding velocity, 0.7 millimeter per minute; temperature, 23° C; and pressure, 1.33×10^{-8} newton per square meter (10^{-10} torr). Oxygen bombardment at 10 micrometers for 30 minutes with 1000-volt potential. Reacted film formed in oxygen at 500° C for 30 minutes.

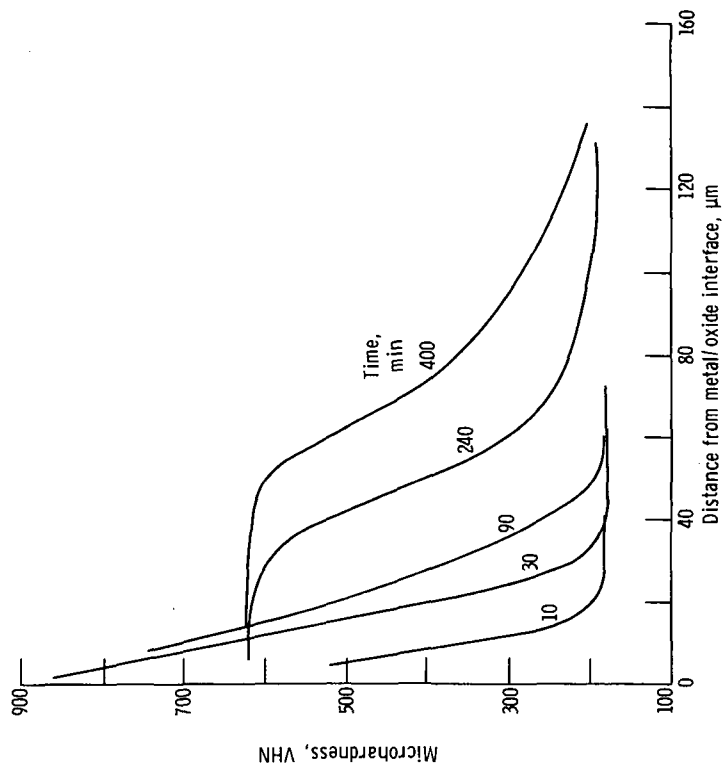


Figure 4. - Microhardness traverses on cross section of titanium specimens oxidized for various lengths of time at 900° C and 1×10^5 newtons per square meter oxygen (ref. 3).

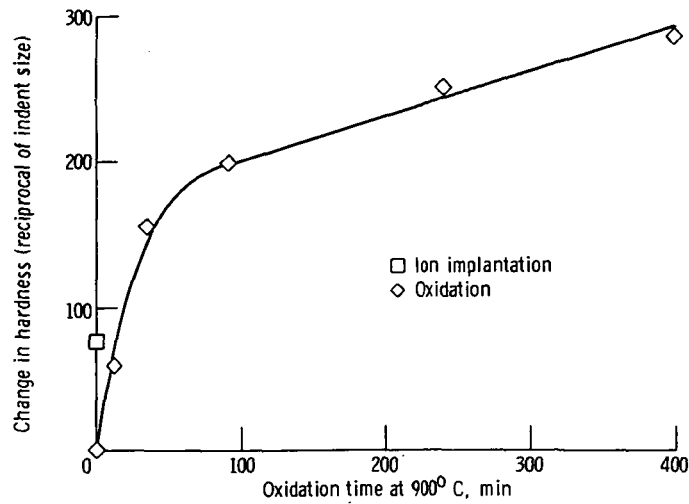


Figure 5. - Influence of oxygen diffusion by oxidation and oxygen ion bombardment on change in surface microhardness of titanium.

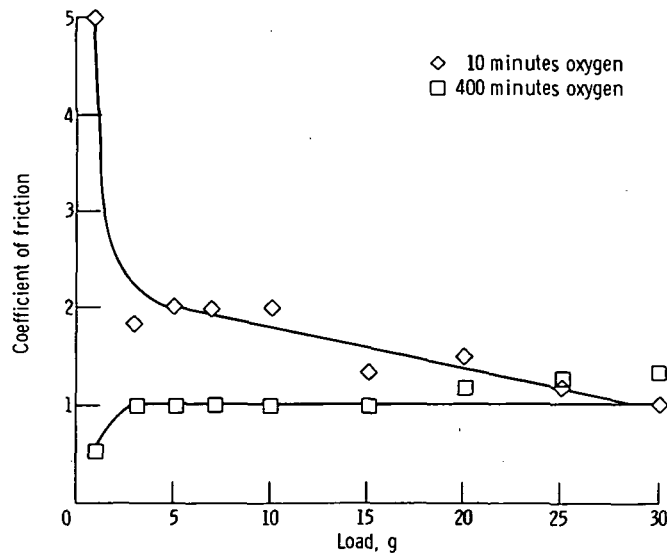


Figure 6. - Coefficient of friction for single crystal of gold (111) sliding on single crystal of titanium (0001). Sliding velocity, 0.7 millimeter per minute; temperature, 23°C; and pressure, 1.33×10^{-8} newton per square meter (10^{-10} torr). Titanium surface oxidized by exposure to oxygen at 1×10^5 newtons per square meter with a specimen temperature of 900°C. Oxide scale removed.

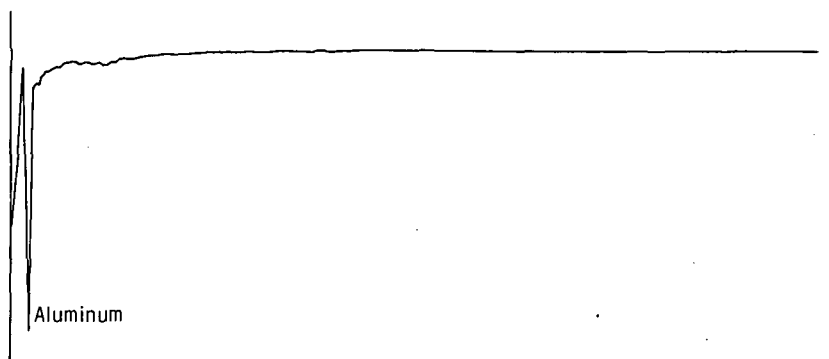
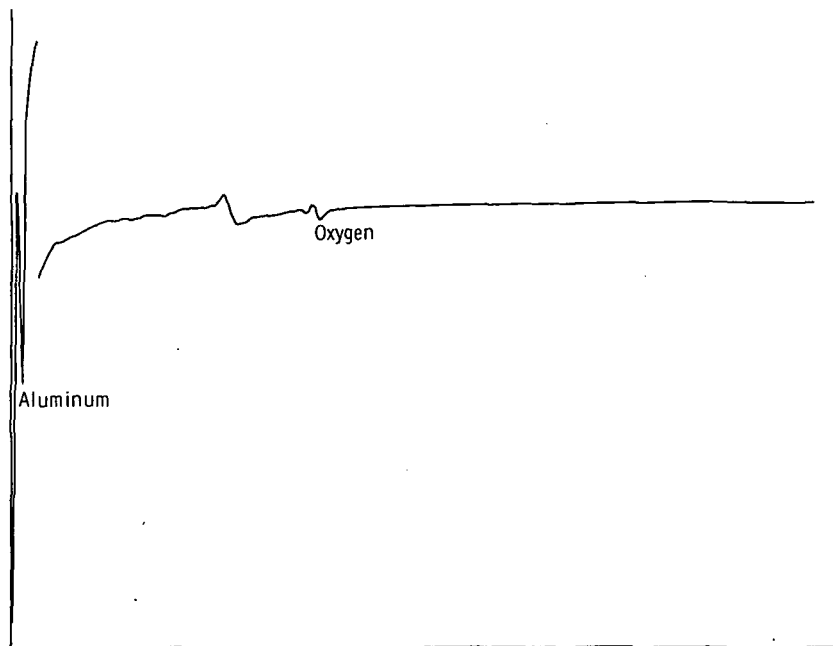
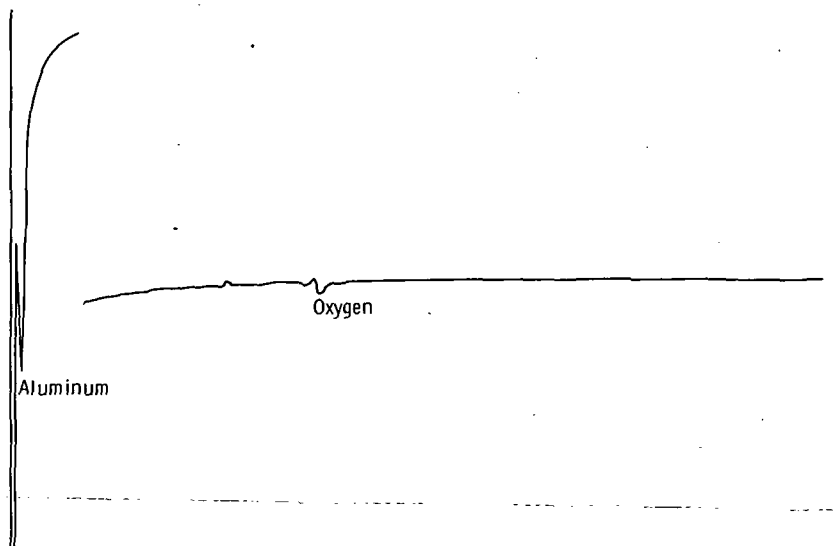


Figure 7. - Auger electron spectroscopy spectrum for argon sputter cleaned aluminum. Argon pressure of 10 micrometers with 1000-volt potential and 30 minutes of bombardment.



(a) Heated in oxygen at 500° C for 30 minutes.



(b) Bombarded with oxygen ions for 30 minutes at 10 micrometers and 1000 volts.

Figure 8. - Auger electron spectroscopy spectrum for aluminum.

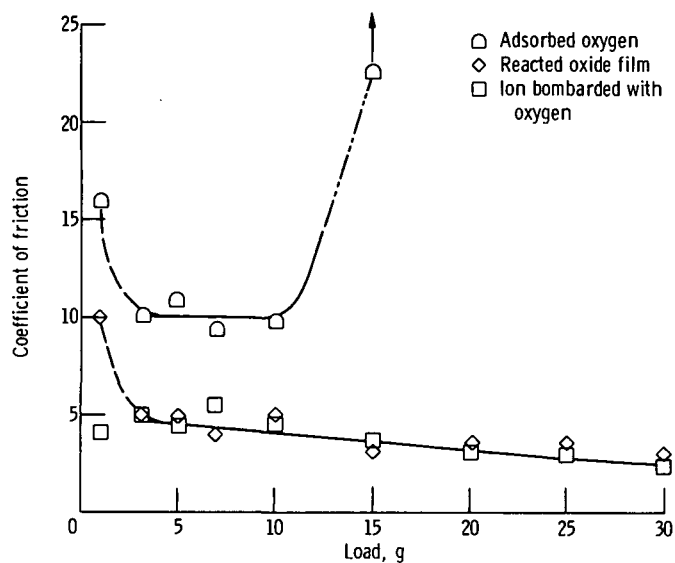


Figure 9. - Friction coefficient at various loads for aluminum given three different types of oxygen exposure. Sliding velocity, 0.7 millimeter per minute; temperature, 23° C; and pressure, 1.33×10^{-8} newton per square meter (10^{-10} torr). Oxygen ion bombardment at 10 micrometers for 30 minutes with 1000-volt potential.

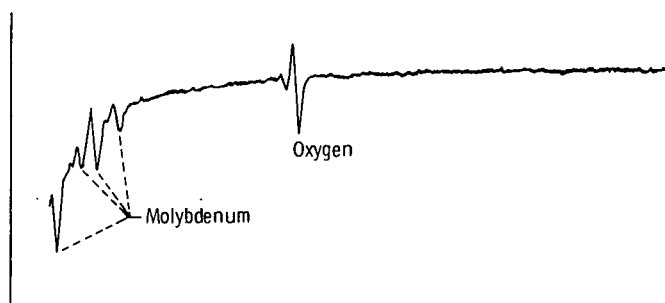


Figure 10. - Auger electron spectroscopy spectrum for molybdenum ion bombarded with oxygen ions. Bombardment pressure 10 micrometers for 30 minutes with 1000-volt potential.

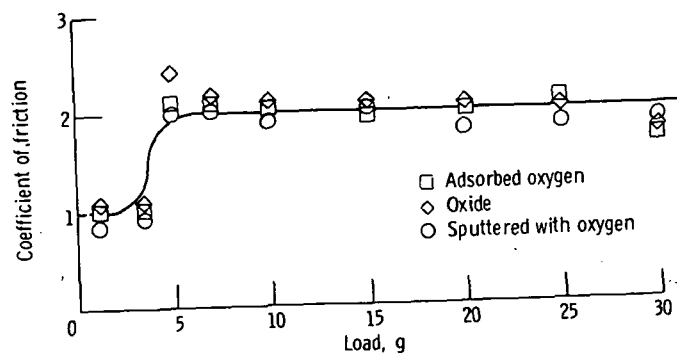


Figure 11. - Coefficient of friction at various loads for molybdenum single crystal surface. Sliding velocity, 0.7 millimeter per minute; temperature, 23° C; and pressure, 1.33×10^{-8} newton per square meter (10^{-10} torr). Surface treated with oxygen by three different mechanisms.

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